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ON THE ADDITION OF ORGANIC ACIDS TO UNSATURATED HYDROCARBONS

BY

ARTHUR F. SIEVERS

A THESIS PRESENTED FOR THE DEGREE OF BACHELOR OF SCIENCE
THE UNIVERSITY OF WISCONSIN
1909

CONTRIBUTIONS FROM THE COURSE IN PHARMACY

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ON THE ADDITION OF ORGANIC ACIDS TO UNSATURATED HYDROCARBONS

INTRODUCTION

With the exception of the polymerization of acetylene and its homologues, no systematic study appears to have been made of the additive capacity of unsaturated hydrocarbons in so far as other carbon compounds are involved.

Inasmuch as a number of observations and experiments, that have been made in this laboratory from time to time, have led up to the present systematic study of this subject, the more significant ones may here be recorded:

In 1894 Mayer [1] made some observations on the angle of rotation of limonene in various optically inactive solvents. He drew the following conclusions from his results: "It is apparent that the solvents employed, viz.: absolute and ordinary alcohol, chloroform and glacial acetic acid, diminish the rotary power of limonene. In the case of absolute alcohol and chloroform the rotatory power of the limonene seems to decrease with fair regularity as the quantity of solvent increases. In the case of glacial acetic acid no such regularity is apparent."

These observations were pursued somewhat farther by Schreiner and Neumann.[2] Inasmuch as the results obtained have never been published, some of them may here be recorded. The experiments were begun by Neumann during the academic year 1900–1901, redeterminations being made by Schreiner in 1902. While the seal of most of the bottles in which these solutions were kept had been injured, some of them were still perfect.

[1] *Am. Chem. Journ.*, 17, p. 692.
[2] E. C. Neumann: *Thesis submitted for the degree of Graduate in Pharmacy, U. W.*, 1901.

It was possible therefore to supplement the observations of Neumann extending over but a few months by observing the angle of rotation after a lapse of five years. This was done, and the following data were obtained, which, for the sake of comparison, are placed side by side with those obtained by Neumann and Schreiner.

Solution	1901	1902	1907
Pure Limonene	104.80	102.00	104.60
Limonene + acetone	36.50	35.00	35.10
Limonene + chloroform	37.14	35.90	35.90
Limonene + ether	36.80	34.30	33.66
Limonene + alcohol	32.30	32.60	28.20
Limonene + glacial acetic acid	34.90	35.40	36.40
Turpentine oil + absolute alcohol	6.71	6.80	6.00

In 1897, at a time when the method of assaying alcoholic components of volatile oils by the acetylization method had come into general use, Professor Kremers became interested in the problem of the influence of the unsaturated hydrocarbons present on the result of the assay. Even if it were not regarded probable that the acetic acid anhydride used in the assay should add to the hydrocarbon, acetic acid might, as had indeed been shown.[3] Inasmuch as most volatile oils contain some moisture the conversion of at least a small part of the acetic acid anhydride to anhydrous acetic acid could be explained. In oils rich in alcohol such a change might become the cause of an insignificant error, but how in oils with but a low alcohol content?

With such a priori conceptions, the results obtained by actual tests were astounding. Preliminary experiments were made with limonene, pinene and caryophyllene. A mixture of 10 cc of the hydrocarbon, 10 cc of acetic acid anhydride and 2 gms. of anhydrous sodium acetate were heated for one hour and then treated according to the usual acetylization method. The results obtained by Martha M. James at that time are herewith recorded:

[3] Bouchardat et Lafont, *Compt. rend.*, 102, p. 171.

Description of hydrocarbon	Amount of ester calculated as $C_{10}H_{17}O.COCH_3$	
	I	II
Limonene from oil of Sweet Orange. Fraction 174°–176°	29.35	29.1
Turpentine—commercial, crude	4.0	3.8
Turpentine, rectified	3.9	3.6
Turpentine—rectified and dried with calcium chloride	2.4	2.7
Turpentine—rectified, dried with calcium chloride and fractionated (150°–156°)	3.3	

These results were so striking that they were stated to Dr. C. Kleber and Dr. Best during the summer of 1896 while Professor Kremers was in the factory of Fritzsche Bros. at Garfield, for the purpose of studying some of the practical problems that presented themselves in the revision of the U. S. P. tests on volatile oils. These gentlemen were naturally skeptical, but their curiosity was sufficiently roused to test the matter. Having on hand a carefully fractionated pinene prepared some months previously and kept in a cool dark cellar, Dr. Best obtained results much higher than those obtained by Miss James for the same hydrocarbon.

Not satisfied, Professor Kremers requested Mr. J. A. Anderson to repeat some of the experiments previously made by Miss James. His results are herewith recorded:

Description of Hydrocarbon	Amount of Ester Calculated as $C_{10}H_{17}O.COCH_3$	
	I	II
Limonene — fraction 174°–178°	50.16	49.5
Limonene — fraction 176°–178°	62.7	65.2
Turpentine oil — crude	7.51	7.33

Before proceeding to record the results of more systematic experimentation, it will be necessary briefly to review the work that has thus far been recorded on this subject. The results found may be briefly summarzied by tabulating the unsaturated hydrocarbons and the organic compounds that have been added to each of these.

PINENE

I. Alcohols
   1) Trinitrophenol
II. Aldehydes
   1) Formaldehyde
III. Acids
   1) Acetic acid
   2) Benzoic acid
   3) Oxalic acid

LIMONENE AND DIPENTENE

I. Alcohols
II. Aldehydes
   1) Formaldehyde
III. Acids

CAMPHENE

I. Alcohols
II. Aldehydes
III. Acids
   1) Formic acid
   2) Acetic acid

FENCHENE

I. Alcohols
   1) Ethyl alcohol
II. Aldehydes
III. Acids
   1) Acetic acid

If, finally, it be borne in mind that some of the processes patented for the semi-artificial preparation of camphor involve the addition of organic acids to the pinene of turpentine oil, it must become apparent that there exist abundant reasons, both purely theoretical as well as practical, which seem to demand a careful and systematic study of the entire problem of the addition of organic compounds, more particularly of organic acids, to unsat-

urated hydrocarbons. A beginning has been made and the results thus far obtained not only justify the time spent on this problem, but invite a much more extensive investigation of the entire field.

THE ADDITION OF GLACIAL ACETIC ACID TO DEXTRO PINENE

The pinene used in the following experiments was obtained from commercial American oil of turpentine. The oil was first rectified by shaking with an aqueous solution of caustic potash and subsequent distillation. The first three-fourths of the oil thus rectified were then fractionated into five fractions and the specific gravity and angle of rotation of the three pinene fractions taken. The results of the fractionation are herewith tabulated.

Fraction	$(D)_{20°}$	$(\alpha)_{20°}$
1. —155°		
2. 155°—156°	0.8560	+15° 50′
3. 156°—157°	0.8564	+14° 14′
4. 157°—160°	0.8585	+11° 41′
5. 160°+		

For the following experiments fractions 2 and 3 were used. They were mixed and their physical constants retaken. These were found to be as follows: Sp. gr. at 20° C. 0.8575; angle of rotation at 20° C + 15° 0′.

500 cc. of this pinene mixture were mixed with an equal volume of glacial acetic acid. At the same time another 500 cc. of the pinene were mixed with two volumes of glacial acetic acid. The physical constants of both mixtures were immediately taken. After that the constants were taken every ten days for some time, but the changes were so small that they were finally taken only once a month.

TABLE I

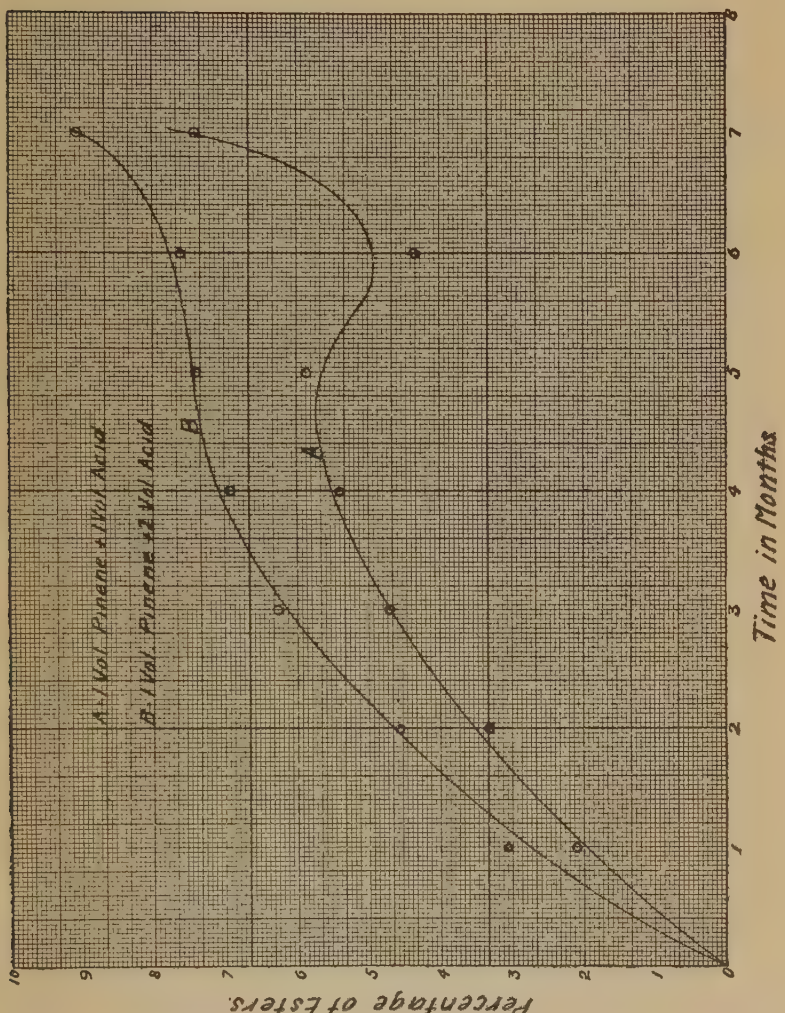
1 Volume of Pinene + 1 Volume of Acid

Date	$(D)_{20°}$	$(\alpha)_{20°}$	Ester No.	p. c. of ester	p. c. as ester
1906					
Aug. 27	0.9400	+8° 41′			
Sept. 21	0.9400	+8° 35′			
Oct. 5	0.9430	+8° 14′			
Oct. 12	0.9428	+8° 15′			
Oct. 22	0.9457	+7° 35′			
Nov. 1	0.9450	+7° 50′	3.92	1.36	2.09
Nov. 11	0.9454	+7° 40′			
Nov. 21	0.9463	+7° 54′			
Dec. 3	0.9464	+7° 32′			
Dec. 13	0.9460	+7° 45′	6.26	2.18	3.32
1907					
Jan. 3	0.9477	+7° 30′			
Jan. 13	0.9477	+7° 20′	8.75	3.06	4.69
Feb. 13	0.9480	+7° 10′	9.97	3.49	5.46
Mar. 15	0.9497	+7° 12′	10.85	3.79	5.82
Apr. 16	0.9500	+7° 20′	8.15	2.86	4.36
May 15	0.9502	+7° 18′	13.80	4.84	7.40

TABLE II

1 Volume of Pinene + 2 Volumes of Acid

Date	$(D)_{20°}$	$(\alpha)_{20°}$	Ester No.	p. c. of ester	p. c. as ester
1906					
Aug. 27	0.9744	+6° 8′			
Sept. 21	0.9744	+6° 6′			
Oct. 5	0.9757	+5° 38′			
Oct. 12	0.9757	+5° 15′			
Oct. 22	0.9767	+4° 50′			
Nov. 1	0.9769	+4° 50′	3.62	1.27	3.03
Nov. 11	0.9770	+4° 47′			
Nov. 21	0.9789	+4° 45′			
Dec. 3	0.9783	+4° 46′			
Dec. 13	0.9785	+4° 35′	5.80	2.03	4.83
1907					
Jan. 3	0.9797	+4° 28′			
Jan. 13	0.9788	+4° 30′	7.46	2.61	6.27
Feb. 13	0.9795	+4° 20′	7.94	2.78	6.58
Mar. 13	0.9814	+4° 17′	8.87	3.10	7.41
April 16	0.9806	+4° 18′	9.15	3.20	7.60
May 15	0.9804	+4° 15′	10.37	3.80	9.05


A-1 Vol. Pinene + 1 Vol. Acid.
B-1 Vol. Pinene + 2 Vol. Acid
A
B
Time in Months
Percentage of Esters.

THE ADDITION OF GLACIAL ACETIC ACID TO DEXTRO LIMONENE

Preparation of Material

The limonene used in the following work was received through the liberality of Dr. S. H. Baer, at that time with Mergentine & Lamm of New York, who had obtained it as by-product in the preparation of a concentrated oil of orange from a crude oil of orange.

The specific gravity in 1906 was 0.8530 at 20° C.; the angle of rotation + 87° 45′ at 20° C.; saponification number 11.84, and acetylization number 26.6.

A small portion of the material was reserved. The bulk of the crude limonene was subjected to a thorough purification. It was first shaken several times with several portions of sodium acid sulphite solution to remove any aldehydes. However the odor of the limonene underwent no perceptible change due to this treatment. In order to determine whether any traces of aldehyde had been removed, the sulphite solution was neutralized with an excess of sodium carbonate and distilled. The distillate had a very decided odor of citronellal. In order to get a positive test for aldehyde the distillate and also the residue were shaken out with ether separately and the ethereal solutions mixed. These upon evaporation left a small quantity of a heavy, syrupy, brown liquid which gave a positive test for aldehyde with magenta solution.

After the removal of the aldehydes the sp. gr. was found to be 0.8562 at 20° C.; the angle of rotation + 92° 47′ at 20° C.; and the saponification number 6.9 and 6.23 respectively.

Since the saponification number of the limonene indicated an appreciable quantity of esters, it was deemed best to saponify the entire quantity. The necessary quantity of caustic potash calculated from the saponification number was dissolved in alcohol and mixed with the limonene. The mixture was then boiled on a water bath for two hours. After cooling the limonene was distilled over with steam. A perfectly clear, colorless prod-

uct was obtained whereas the crude product had been decidedly yellow.

The constants of the limonene thus rectified were found to be: sp. gr. 0.8440 at 20° C.; angle of rotation +96° 37′ at 20° C.; acetylization number 10.1.

The rectified limonene was fractionated into four fractions. The specific gravity and the angle of rotation were taken of each fraction. The following tabulation gives a summary of the fractionation, the constants, and the volume of each fraction.

Fraction	Volume in cc	$(D)_{20°}$	$(\alpha)_{20°}$
— 175°	88	0.8413	+93° 49′
175° — 176.5°	1108	0.8434	+98° 15′
176° — 180°	476	0.8455	+98° 51′
180°+	74	0.8723	+81° 0′

For the sake of better comparisons the data obtained in the several experiments described above are herewith tabulated again:

Description of limonene	$(D)_{20°}$	$(\alpha)_{20°}$	Sap. No.	Ester No.
Crude	0.8530	+87° 45′	11.45	26.6
Shaken out with $NaHSO_3$	0.8562	+92° 47′	6.56	.....
Saponified	0.8440	+96° 37′	4.0*	10.1
Fraction — 175°	0.8413	+93° 49′	3.16*	.....
Fraction 175°—176.5°	0.8434	+98° 15′	2.65*	7.6
Fraction 176.5°—180°	0.8455	+98° 51′	1.30*	14.4
Fraction 180°+	0.8723	+81° 0′	5.06*	51.00

* Determinations made five weeks after rectification and fractionation.

Formation of the Esters

In the experiments which follow the limonene from fraction 175°-176.5° was used. The object was to ascertain the rate of ester formation of the limonene with the glacial acetic acid, and the extent to which this formation is indicated by the specific gravity and the angle of rotation of the mixture.

Two different mixtures of the limonene and the glacial acetic acid were made. The first mixture consisted of one volume of limonene and one volume of glacial acetic acid. The second mix-

ture consisted of one volume of limonene and two volumes of the acid.

To determine the effect of so-called catalytic agents on the rate of ester formation in these mixtures, four more mixtures were made, two containing hydrogen chloride and two anhydrous sodium acetate.

The two mixtures containing sodium acetate were prepared as the previous ones, namely: one containing equal volumes of limonene and glacial acetic acid and the other containing one volume of limonene to two of the acid. To each of these mixtures were then added exactly 2.5 gms. of anhydrous sodium acetate and the mixtures agitated frequently until the acetate was dissolved.

Two more mixtures were prepared to each of which were added the molecular equivalent of 2.5 gms. of anhydrous sodium acetate or 1.11 gms. of hydrogen chloride. In all these mixtures great care was taken to prevent any admixtures of traces of moisture. It was, therefore, necessary to add the hydrogen chloride in some anhydrous form and not in the form of the ordinary aqueous test solution. The method adopted was as follows: Hydrogen chloride was generated from common salt with sulphuric acid and passed first through a wash bottle containing sulphuric acid, and then through a bottle with calcium chloride. The gas, which after this treatment was regarded as dry, was then passed into glacial acetic acid. The percentage of hydrogen chloride in the acid was then determined gravimetrically with silver nitrate as insoluble silver chloride.

A quantity of this acid containing exactly 1.11 gms. of hydrogen chloride was weighed off, diluted to the desired volume and mixed with the limonene as in the previous mixtures.

The specific gravity and angle of rotation of these mixtures were taken immediately after they had been mixed and after that, with as much regularity as possible, at intervals of ten days. The changes found in the constants in ten days were so small, however, that they were finally taken only once a month. Once during each month of observation the amount of ester formed was determined by means of the acetylization number.

In determining the acetylization number considerable difficulty

was met with at first due to the strong acetic acid solution. After considerable experimentation the following method was found to give very accurate results: About 8 gms. of the mixture are weighed carefully and then transferred to a 250 cc. flask and a few drops of phenolphthalein added. An alcoholic potassium hydroxide solution containing about 50 gms. of potassium hydroxide to the liter is then added slowly to neutralize the acetic acid. The flask must be kept carefully cooled during the addition of the alkali in order to prevent the decomposition of any esters due to a rise in temperature. When exactly neutral, 10 cc. of a standard alcoholic potassium hydroxide solution are added and the mixture boiled for half an hour on a water bath. After cooling the excess of alkali is titrated back with ½ N. Sulphuric Acid V. S.

TABLE I

1 VOLUME OF LIMONENE + 1 VOLUME OF ACID

Date	$(D)_{20°}$	$(\alpha)_{20°}$	Ester No.	p. c. of ester	p. c. as ester
Nov. 29, 1906.....	0.9380	+47° 30′	.....	.....	.....
Dec. 8, 1906.....	0.9384	+47° 45′	.....	.....	.....
Dec. 18, 1906.....	0.9390	+47° 33′	.....	.....	.....
Jan. 4, 1907.....	0.9388	+47° 10′	1.84	0.64	1.00
Feb. 12, 1907.....	0.9390	+47° 45′	3.35	1.17	1.80
Mar. 15, 1907.....	0.9392	+47° 32′	3.37	1.18	1.82
Apr. 15, 1907.....	0.9398	+47° 30′	3.86	1.35	2.09
May 15, 1907.....	0.9400	+47° 0′	3.81	1.33	2.06

TABLE II

1 VOLUME OF LIMONENE + 2 VOLUMES OF ACID

Date	$(D)_{20°}$	$(\alpha)_{20°}$	Ester No.	p. c. of ester	p. c. as ester
Nov. 29, 1906.....	0.9733	+31° 52′	.....	.....	.....
Dec. 8, 1906.....	0.9733	+31° 45′	.....	.....	.....
Dec. 18, 1906.....	0.9730	+31° 25′	.....	.....	.....
Jan. 4, 1907.....	0.9737	+31° 0′	1.07	0.37	0.89
Feb. 12, 1907.....	0.9828	+31° 15′	2.03	0.71	1.70
Mar. 15, 1907.....	0.9744	+31° 25′	3.35	1.17	2.84
Apr. 15, 1907.....	0.9755	+31° 35′	3.35	1.17	2.84
May 15, 1907.....	0.9748	+31° 43′	3.26	1.14	2.74

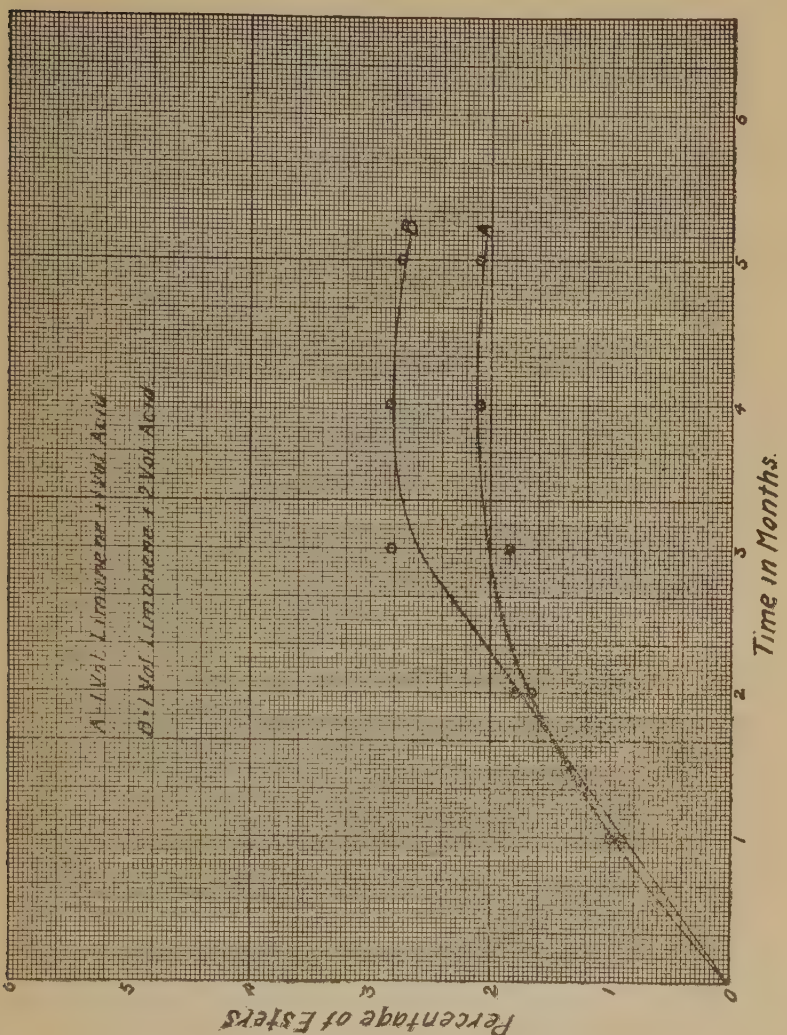

A: 1 Vol. Limonene + 1 Vol. Acid
B: 1 Vol. Limonene + 2 Vol. Acid
Percentage of Esters
Time in Months.
0
1
2
3
4
5
6

TABLE III

1 VOLUME OF LIMONENE + 1 VOLUME OF ACID + 1.11 GMS. OF HCl

Date	$(D)_{20°}$	$(\alpha)_{20°}$	Ester No.	p. c. of ester	p. c. as ester
1906					
Nov. 29	0.9390	+47° 35′	.....	.....	.....
Dec. 8	0.9389	+48° 00′	.....	.....	.....
Dec. 18	0.9390	+47° 40′	.....	.....	.....
1907					
Jan. 4	0.9403	+47° 20′	3.00	1.08	1.68
Feb. 12	0.9430	+46° 40′	3.50	1.22	1.92
Mar. 15	0.9402	+47° 38′	5.41	1.89	2.93
Apr. 15	0.9441	+47° 34′	4.20	1.47	2.28
May 15	0.9408	+46° 45′	5.09	1.78	2.78

TABLE IV

1 VOLUME OF LIMONENE + 2 VOLUMES OF ACID + 1.11 GMS. OF HCl

Date	$(D)_{20°}$	$(\alpha)_{20°}$	Ester No.	p. c. of ester	p. c. as ester
1906					
Nov. 29	0.9742	+31° 50′	.....	.....	.....
Dec. 8	0.9740	+31° 37′	.....	.....	.....
Dec. 18	0.9740	+31° 20′	.....	.....	.....
1907					
Jan. 4	0.9750	+31° 30′	2.65	0.92	2.23
Feb. 12	0.9746	+31° 15′	3.61	1.26	3.04
Mar. 15	0.9750	+31° 20′	3.73	1.30	3.14
Apr. 15	0.9764	+31° 35′	3.92	1.37	3.30
May 15	0.9754	+31° 25′	4.49	1.57	3.78

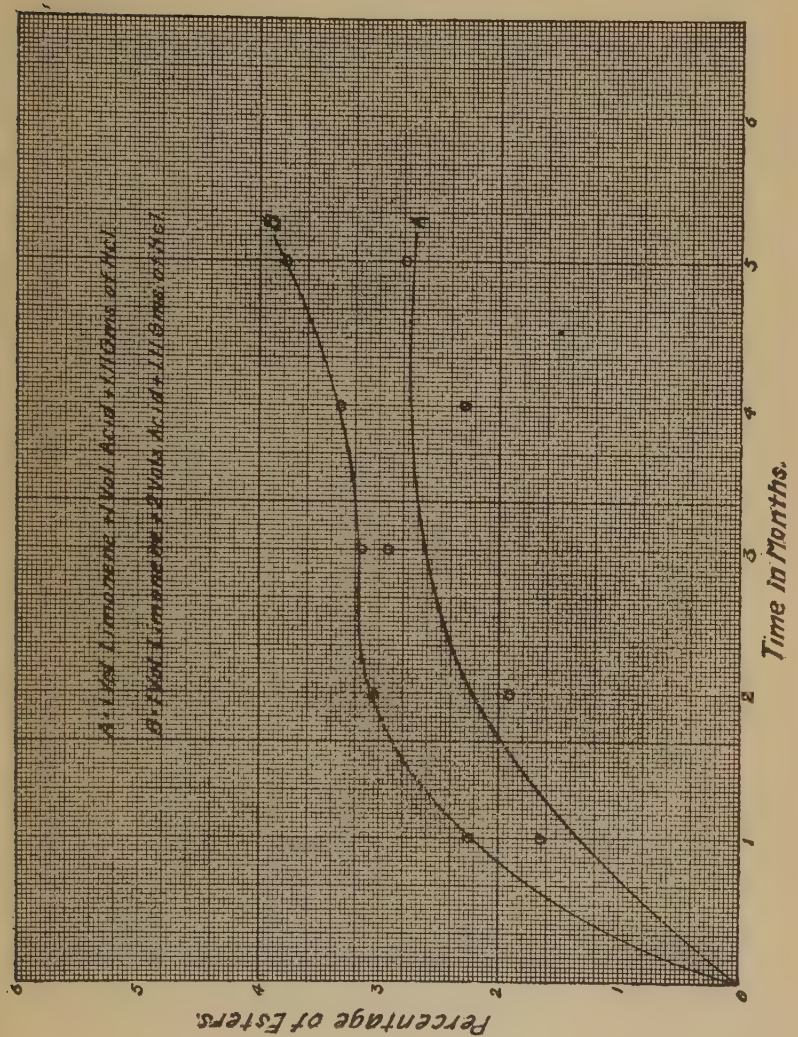

A. 1 Mol. Limonene + 1 Mol. Acid + 1.1 Grms. of Hol.
B. 1 Mol. Limonene + 2 Mols. Acid + 1.1 Grms. of Hol.
Time in Months.
Percentage of Esters.

TABLE V

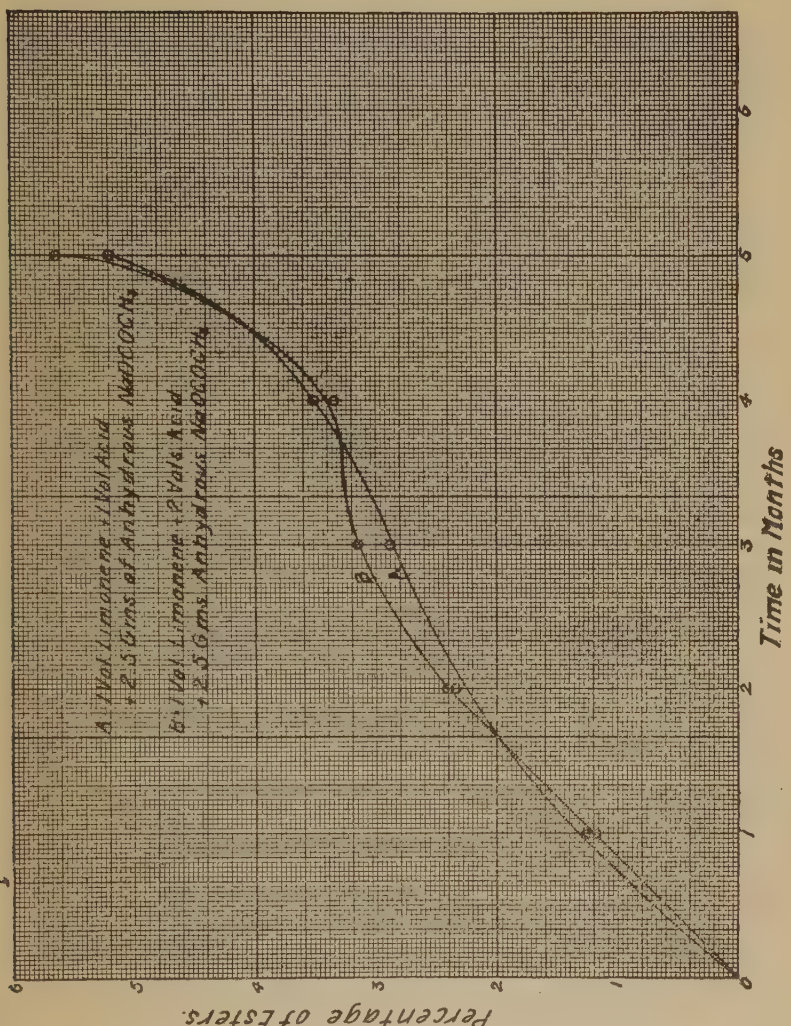
1 VOL. OF LIMONENE+1 VOL. OF ACID+2.5 GMS. OF ANHYD. Na $OCOCH_3$

Date	$(D)_{20°}$	$(\alpha)_{20°}$	Ester No.	p. c. of ester	p. c. as ester
1906					
Nov. 29	0.9414	+47° 40′			
Dec. 8	0.9416	+47° 37′			
Dec. 18	0.9430	+46° 45′			
1907					
Jan. 4	0.9440	+46° 25′	2.21	0.77	1.26
Feb. 12	0.9453	+46° 15′	4.32	1.51	2.35
Mar. 15	0.9464	+46° 0′	5.32	1.86	2.88
Apr. 15	0.9482	+45° 50′	6.49	2.27	3.55
May 15	0.9490	+45° 15′	9.47	3.32	5.19

TABLE VI

1 VOL. OF LIMONENE+2 VOLS. OF ACID+2.5 GMS. OF ANHYD. Na $OCOCH_3$

Date	$(D)_{20°}$	$(\alpha)_{20°}$	Ester No.	p. c. of ester	p. c. as ester
1906					
Nov. 29	0.9758	+31° 50′			
Dec. 8	0.9764	+31° 40′			
Dec. 18	0.9767	+31° 30′			
1907					
Jan. 4	0.9758	+31° 4′	1.40	0.49	1.18
Feb. 12	0.9770	+31° 20′	2.85	0.99	2.40
Mar. 15	0.9785	+31° 0′	3.73	1.30	3.15
Apr. 15	0.9800	+31° 5′	3.94	1.38	3.33
May 15	0.9798	+31° 12′	6.75	2.36	5.70


A 1 Vol. Limonene + 1 Vol. Acid + 2.5 Grms. of Anhydrous NaOOCH3
B 1 Vol. Limonene + 2 Vols. Acid + 2.5 Grms. Anhydrous NaOOCH3
Time in Months
Percentage of Esters.

Formation of Esters at Higher Temperatures and Under Increased Pressure

In order to determine the effect of higher temperature and increased pressure the following experiments were conducted: Two mixtures of pinene and glacial acetic acid, one containing equal volumes of both, and the other one volume of pinene and two volumes of the acid, were placed in small pressure bottles and heated in a water bath. After heating for eight hours the physical constants and ester content were determined. Fresh mixtures were then heated under the same conditions for sixteen hours and the physical constants and ester content again determined. Finally similar mixtures were heated for twenty-four hours.

The temperature, 100° C., applied in this case was below the boiling point of the mixture, and as the amount of ester obtained was not very great, further experiments were performed with the same material in which higher temperatures were applied. In this case the bottles containing the mixtures were heated in an oil-bath at a temperature ranging from 140°-150° C. This temperature was chosen because it is above the boiling point of the glacial acetic acid and also above that of the mixture, whereas it is below that of the pinene. The time of heating was, as in the previous experiments, eight, sixteen, and twenty-four hours respectively.

The mixtures heated at the higher temperatures acquired a light straw color when heated for sixteen hours and a decided yellow color when heated for twenty-four hours.

The following tabulation shows the results obtained in the three different series of experiments.

TABLE I. 100° C

1 Volume of Pinene + 1 Volume of Acid

Time	$(D)_{20°}$	$(\alpha)_{20°}$	Ester No.	p. c. of ester	p. c. as ester
8 hrs	0.9465	+4° 25′	10.18	3.77	5.80
16 hrs	0.9488	+3° 36′	13.80	4.83	7.42
24 hrs	0.9502	+3° 40′	15.54	5.44	8.37
1 Volume of Pinene + 2 Volumes of Acid					
8 hrs	0.9807	+2° 33′	10.30	3.60	8.58
16 hrs	0.9823	+2° 33′	14.43	5.05	12.10
24 hrs	0.9838	+2° 36′	15.70	5.49	13.12

TABLE II. 140° to 150° C

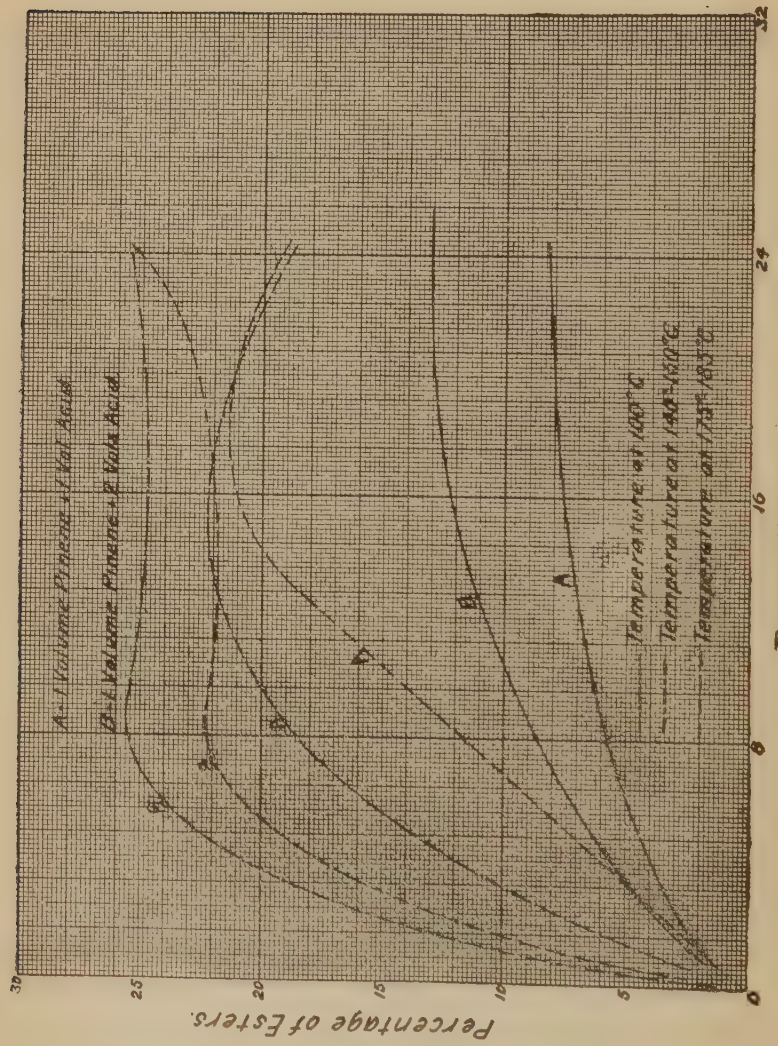
1 Volume of Pinene + 1 Volume of Acid

Time	$(D)_{20°}$	$(\alpha)_{20°}$	Ester No.	p. c. of ester	p. c. as ester
8 hrs	0.9590	+4° 24′	34.50	12.09	18.78
16 hrs	0.9586	+4° 0′	40.90	14.30	22.26
24 hrs	0.9568	+3° 52′	34.92	12.21	18.90
1 Volume of Pinene + 2 Volumes of Acid					
8 hrs	0.9962	+2° 35′	30.10	10.52	25.50
16 hrs	0.9921	+2° 20′	29.45	10.30	24.80
24 hrs	0.9881	+1° 30′	30.20	10.58	25.40

TABLE III. 175° to 185° C

1 Volume of Pinene + 1 Volume of Acid

Time.	$(D)_{20°}$	$(\alpha)_{20°}$	Ester No.	p. c. of ester	p. c. as ester
8 hrs	0.9517	+3° 0′	21.12	7.39	11.5
16 hrs	0.9509	+3° 25′	39.4	13.8	21.00
24 hrs	0.9581	+3° 18′	35.10	12.13	19.1
1 Volume of Pinene + 2 Volumes of Acid					
8 hrs	0.9895	+2° 37′	26.58	9.31	11.5
16 hrs	0.9873	+3° 3′	26.1	9.14	21.97
24 hrs	0.9876	+1° 23′	30.10	10.52	25.3


A. Volume Phenol + Vol. Acid.
B. Volume Ethene + 2 Vols Acid
Temperature at 100°C
Temperature at 140°C
Temperature at 175°C
Percentage of Esters.
Time in Hours
0
5
10
15
20
25
30
8
16
24
32

ESTER FORMATION UNDER ORDINARY PRESSURE

The preceding experiments show the extent of ester formation when the mixtures are heated in sealed tubes at various temperatures and for various intervals of time. In order to study the effect of the time of heating under normal pressure the following series of experiments were conducted. 300 cc. of a mixture of equal parts of pinene and glacial acetic acid were placed in a round bottomed flask of one liter capacity and connected with a reflux condenser. The mixture was heated slowly up to its boiling point when the heat was removed long enough to take a small sample from the flask. The heating was then continued for fifteen minutes when another sample was removed. In this way the experiment was continued, samples being taken out at definite intervals, such intervals being gradually increased as the heating continued. Towards the last the samples were taken out every two hours. Altogether the mixture was heated twenty hours. As the heating proceeded the material in the flask gradually darkened and at the close of the period had acquired a dark brown color.

The samples taken out in each case were just enough for one ester determination. No duplicate could therefore be made; neither could the specific gravity and angle of rotation be taken of each sample. The specific gravity and optical rotation of the mixture before heating were taken and found to be as follows, viz.: sp. gr. at $20°=0.9400$; angle of rotation at $20°=+8°\ 40'$.

After heating for twenty hours the specific gravity was found to be 0.9529 at 20° C. The optical rotation could not be taken on account of the dark color of the mixture.

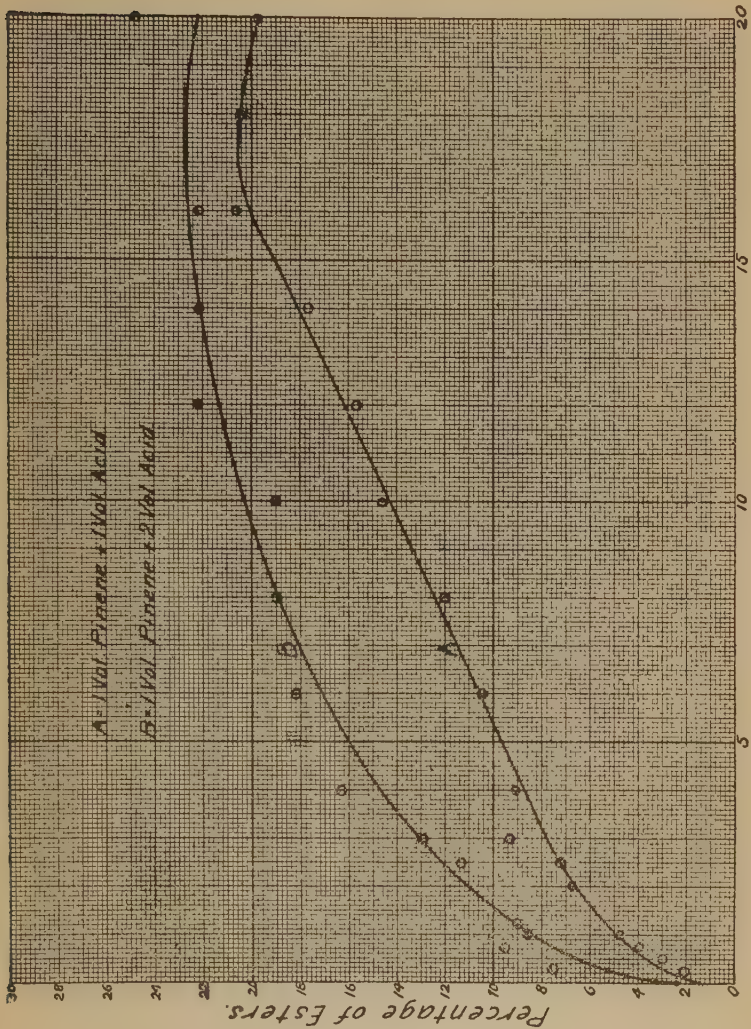
An exact duplicate of this experiment was made with a mixture of one volume of pinene and two volumes of glacial acetic acid. Samples were taken out at exactly the same intervals and the heating carried out under exactly the same conditions. In this case again the mixture gradually turned dark and after twenty hours of heating it also was of a dark reddish-brown color, slightly darker, however, than the preceding mixture.

The physical properties before heating were as follows: specific gravity at 20° C.= 0.9745; optical rotation at 20° C. =+6° 8′. After heating the specific gravity was 0.9888. Here again the optical rotation could not be taken on account of the dark color of the mixture.

The boiling point of the first mixture was 116.5° C. and that of the second was 116° C. In both cases the boiling point rose very gradually through about one degree during the process of heating.

The following is a tabulation of the ester number, percentage of ester, and percentage of pinene as ester in each sample. In order to calculate the true percentage of pinene as ester in the mixture it is necessary to know the specific gravity in each case. Since the specific gravity was not taken in each case the average of the specific gravities of the mixtures before and after heating was used in the calculations. It must therefore be borne in mind that the percentage as tabulated below is only a very close approximation. The average specific gravity of the first mixture was 0.9464 at 20°; that of the second was 0.9815 at 20°.

Time	1 Volume of Pinene + 1 Volume of Acid			1 Volume of Pinene + 2 Volumes of Acid		
	Ester No.	p. c. of ester	p. c. as ester	Ester No.	p. c. of ester	p. c. as ester
	2.56	0.89	1.37	2.90	1.01	2.39
15 min.	3.71	1.29	1.99	9.04	3.16	7.46
30 min.	5.51	1.93	2.96			
45 min.	7.29	2.55	3.91	11.87	4.16	9.81
1 hr.	9.01	3.15	4.82	10.60	3.71	8.75
1:15	19.63	3.36	5.16	10.90	3.81	8.99
1:30				11.95	4.20	9.90
2 hrs.	12.53	4.38	6.71			
2:30	13.30	4.65	7.13	13.50	4.73	11.15
3 hrs.	17.32	6.05	9.28	15.60	5.46	12.90
4 hrs.	16.80	5.89	9.02	19.70	6.90	16.30
6 hrs.	19.60	6.86	10.51	22.00	7.70	18.20
8 hrs.	22.60	7.91	12.10	23.05	8.05	19.00
10 hrs.	28.30	9.55	14.63	23.00	8.05	19.00
12 hrs.	29.30	10.24	15.70	26.80	9.36	22.18
14 hrs.	31.10	10.84	16.68	26.80	9.39	22.18
16 hrs.	38.60	13.32	20.70	26.78	9.37	22.10
18 hrs.	38.05	13.31	20.40	25.20	8.82	20.80
20 hrs.	36.60	12.81	19.61	30.00	10.50	24.80


A: 1 Vol. Pinene + 1 Vol. Acid
B: 1 Vol. Pinene + 2 Vol. Acid
Percentage of Esters.
Time in Hours.
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
5
10
15
20

ADDITION OF PICRIC ACID TO PINENE

Bornyl picrate was prepared according to Tilden and Forster [4] in the following way: 20 gms. of chemically pure picric acid were mixed with 200 cc. of rectified turpentine oil in a round bottomed liter flask connected with a reflux condenser. No reaction was observed in the cold, and the acid, being insoluble in the turpentine oil, settled at the bottom. The temperature was slowly raised by means of a low flame. As the temperature rose the mixture gradually acquired a reddish color which changed to dark red-brown when 150° was reached. At this temperature the mixture began to crack and the evolution of heat was almost sufficient to keep the temperature at 150° without the aid of a flame. After heating for about one hour the mixture was allowed to cool somewhat, after which the liquid portion was poured into a beaker and set aside in a cool place to crystallize. The black tarry residue which remained in the flask was examined later.

After about twelve hours small clusters of crystals began to form on the sides of the beaker containing the liquid, and after twenty-four hours the crystallization was interrupted, the mother liquid set aside for further crystallization, and the crystals removed for purification. On the bottom of the beaker was a layer of tarry material resembling that which remained in the original flask.

The crystals were rubbed in a mortar with several portions of water to remove the picric acid. They were then transferred to a flask and boiled with alcohol until all were dissolved. Upon cooling the crystals again separated in the form of small yellow scales. After draining on a force filter and washing several times with small portions of alcohol, the crystals were allowed to dry and were then transferred to a bottle.

Upon standing in diffused daylight the crystals soon became darker in color, changing from a bright yellow to a yellowish-

[4] *Journ. Am. Chem. Soc.*, 1893 I, p. 1388.

brown. That side of the bottle which was exposed to the direct light of the window changed color much more quickly.

The mother liquid, after standing for several hours, showed no signs of further crystallization and was therefore taken and distilled with steam. A colorless oily layer separated from the aqueous distillate. This material which had a distinct pinene odor was separated and fractionated. It distilled at a temperature ranging from 150° to 159° C., the bulk of it distilling at 155° to 157°. The specific gravity of the main fraction was found to be 0.8599 at 20° C. and the angle of rotation was +5° 40′.

Judging from the odor, boiling point, and specific gravity, the material was pinene with a greatly reduced optical activity.

Saponification of the "Ester"

The bornyl picrate was mixed with a molecular quantity of potassium hydroxide in alcohol and boiled on a water bath for about one hour. The mixture turned to a dark brown color After cooling, the material was distilled with steam. The first distillate consisted mainly of alcohol with a strong camphoracous odor. Upon further distillation small crystals began to separate on the sides of the flask and condenser and also in the receiver. After no more crystals came over the distillation was stopped and the borneol collected and drained on a filter. It consisted of fine white crystals.

ACTION OF GLACIAL ACETIC ACID ON AMYLENE

In order to ascertain whether esters of the unsaturated hydrocarbons of the olefine series could be obtained in like manner, the action of glacial acetic acid on amylene was tried.

The amylene used was optically inactive and had a specific gravity of 0.6779 at 20° C. A mixture of equal volumes of amylene and glacial acetic acid had a specific gravity of 0.8639 at 20° C. immediately after mixing. A mixture of one volume of amylene and two volumes of glacial acetic acid had a specific gravity of 0.9250 at 20° C.

After standing for just one month the ester content was determined by means of a method similar to that used for the other mixtures.

1 VOLUME AMYLENE + 1 VOLUME GLACIAL ACETIC ACID

Date	$(D)_{20°}$	Ester No.	p. c. of ester	p. c. as ester
May 20, 1907.....	0.864	12.86	2.97	7.90
1 VOLUME AMYLENE + 2 VOLUMES GLACIAL ACETIC ACID				
May 20, 1907.....	0.9253	7.97	1.85	7.58

CONCLUSIONS

In summarizing the facts brought out by the foregoing experiments one appears especially significant, namely the influence of the mass. In every experiment performed this is clearly brought out. The percentage of hydrocarbon changed to ester is, with one exception, appreciably higher in each case where the amount of the acid is doubled. In the curves accompanying these data, curve A shows in each case the results obtained from one volume of the hydrocarbon with one volume of the acid, and curve B the results obtained from one volume of the hydrocarbon with 2 volumes of the acid. A study of the curves will show that, with one exception, the percentage of the hydrocarbon changed to ester in mixture B is considerably higher than in mixture A. This increase in ester is apparent in the very first observation made and continues to be so throughout the entire time of observation extending through several months.

Whereas the amount of the acid in B in these experiments was only twice that in A, it is reasonable to suppose that a greater increase in the ratio of acid to hydrocarbon may lead to a still higher percentage of addition products formed. However, this has still to be proven experimentally. It seems safe to say, however, even from the few observations made in regard to the influence of mass action, that, to secure a yield of ester which would be of any practical commercial value, the significance of mass

influence is a very important one, and one which will be deserving of careful consideration.

In the experiments with limonene not only the influence of mass action was observed, but also the influence of so-called catalytic agents. Anhydrous sodium acetate has long been employed in the acetylization of volatile oils by means of acetic acid anhydride. Just what its action is in such cases has never been satisfactorily explained. The fact remains, however, that it insures a more complete esterification. It was interesting, therefore, to try its action in these experiments, where we have ester formation, not by the action of an acid on alcohol as is supposed to be the case in volatile oils, but by direct addition. If in this case an increase of ester could be observed due to the presence of such a reagent then a similar significance might be attached to its use in the determination of alcohols in volatile oils.

Another so-called catalytic agent used was anhydrous hydrogen chloride. The mixtures of limonene and glacial acetic acid were exactly the same in each case and differed only in the presence of these so-called catalytic agents. Any difference in the percentage of hydrocarbon changed to ester can therefore only be accounted for by the action of these agents.

In studying the curves plotted from the data obtained from these experiments some extremely interesting results are brought out. The data thus far recorded have been obtained from observations extending over approximately five months. The first set of curves shows the amount of limonene changed to ester when standing in contact with glacial acetic acid alone. In five months a maximum of 2.84 p. c. was obtained. The second set of curves shows the influence of the anhydrous hydrogen chloride. In this case a maximum of 3.78 p. c. was obtained. The third set of curves shows the influence of the anhydrous sodium acetate. Here a maximum of 5.71 p. c. was observed. Thus we have a difference of 2.86 p. c. due to apparently no other cause than the influence of the sodium acetate, and an increase of 0.94 p. c. due to the influence of the hydrogen chloride. Thus with sodium acetate we have a percentage of ester which is a trifle more than twice that in a similar mixture but without the so-called catalytic agent. From these results it becomes evident

that both the so-called catalytic agents used have a tendency to increase the additive capacity of the hydrocarbon, and that sodium acetate has by far the greater influence of the two. An interesting observation that should be made here is the relation of the presence of sodium acetate to mass action. It will be observed in the first two sets of curves that mixture B shows a considerable increase in percentage over A. In the curves for the mixtures containing sodium acetate, however, both show very nearly the same extent of ester formation. This is true throughout the entire period of observation. The influence of mass action is apparently lost here.

The experiments performed to show the influence of higher temperatures and pressure on the amount of ester formed bring out many points of interest. From the curves it can be seen that the greatest addition takes place during the first eight hours of heating. This is especially true where higher temperatures than 100° are employed. After heating 16 hours there is apparently little or no increase in the addition products formed; in fact in some cases there is a decrease as the curves indicate. In the mixtures containing one volume of pinene to two volumes of glacial acetic acid we practically reach the maximum percentage after the first eight hours of heating.

It must be borne in mind, however, that in these experiments we have entirely different conditions than in those where the time of contact alone becomes a factor. The high temperatures and the correspondingly high pressure under which these data were obtained doubtless give rise to reactions other than the mere addition of the acid to the ester-forming hydrocarbon. Thus there may be a change of the hydrocarbon pinene to its isomer limonene, or other similar reactions. The assumption that such varied, and possibly, highly complex changes take place under the existing conditions gains weight from the fact that the physical constants of these mixtures undergo extensive changes under this treatment. These changes seem to occur with no apparent regularity as is the case with the mixtures standing in simple contact at room temperature.

Viewed from a practical standpoint, it at once becomes apparent that there is no material advantage in prolonging the

time of heating. From the data obtained thus far it seems safe to say that sixteen hours would be quite sufficient. As far as the change of the hydrocarbon to ester is concerned, the greatest efficiency is obtained by heating one volume of pinene with two volumes of glacial acetic acid at 175° to 185° for a period of about eight hours.

The experiments conducted with the object of determining the influence of increased pressure on the amount of ester formation have proved of very great importance. The results have demonstrated without doubt that any increase over normal atmospheric pressure and any temperature above the boiling point is of no material advantage. Thus the maximum percentage of hydrocarbon changed to ester at 175° to 185° is a trifle over 25 per cent after heating for 24 hours, while the maximum percentage obtained when boiling a similar mixture under ordinary pressure for 20 hours is 24.8 per cent. This result when viewed from a practical standpoint is of great significance. Whereas the last experiment is easily conducted, the first involves numerous technical difficulties, at least when conducted on a large scale.

One of the objects in view when these experiments were begun was to determine to what extent the amount of ester formation would be indicated by the physical constants. In the long series of observations on pinene with acetic acid some interesting points have been brought out in regard to the changes in physical constants. The changes were very gradual but after seven or more months of observation, it is found that the specific gravity has increased and the angle of rotation has decreased in both mixtures. With a few exceptions, due probably to experimental error, these changes have proceeded with fair regularity in both mixtures.

In the experiment with limonene we again find the specific gravity slowly increasing with the time of contact. This is especially true in cases where the so-called catalytic agents have been used. The optical activity, however, does not show any changes in any definite direction. In the experiments where higher temperatures and pressure are employed the physical constants, as has been mentioned previously, change back and forth

without any regularity whatsoever. Taken as a whole the changes in the physical constants seem to be too small to serve as a valuable criterion in regard to the amount of ester present.

Finally, in summarizing the results which these experiments have brought out, it must become apparent that the matter under investigation is of sufficient interest, both practically as well as theoretically, to warrant a further systematic study of the subject. In the work here recorded only the action of acetic acid has been studied, but the investigation of the action of other organic acids appears fully as promising.

OBSERVATIONS AND CONCLUSIONS AFTER TWO AND ONE-HALF YEARS

The investigations recorded in the foregoing pages were temporarily brought to a close in June, 1907. The different mixtures of hydrocarbons and acids which had been used were carefully set aside to be examined again some time in the future, if the opportunity presented itself. Such an opportunity came in December, 1909, two and one-half years later. The mixtures were again examined as to specific gravity, angle of rotation, and the amount of esterification. The esters were determined in the same way as in the earlier examinations. In order to show the changes that had taken place in these mixtures since their last previous examination, the following tabulation is appended which shows the results of the last examination in 1907, and the recent one in December, 1909.

PINENE AND GLACIAL ACETIC ACID

Date	1 Vol. of Pinene + 1 Vol. of Acid			1 Vol. of Pinene + 2 Vols. of Acid		
	$D_{20°}$	$(\alpha)_{20°}$	p. c. of pinene as ester	$D_{20°}$	$(\alpha)_{20°}$	p. c. of pinene as ester
May 15, 1907...	0.9502	+7° 18′	7.40	0.9804	+4° 15′	9.05
Dec. 7, 1909....	0.9590	+3° 15′	18.30	0.9960	+2° 15′	28.70

LIMONENE AND GLACIAL ACETIC ACID

Date	1 Vol. of Limonene + 1 Vol. of Acid			1 Vol. of Limonene + 2 Vols. of Acid		
	$D_{20°}$	$(\alpha)_{20°}$	p. c. limonene as ester.	$D_{20°}$	$(\alpha)_{20°}$	p. c. limonene as ester.
May 15, 1907.	0.9400	+47° 0′	2.06	0.9748	+31° 43′	2.74
Dec. 7, 1909.	0.9470	+38° 39′	12.90	0.9880	+28° 42′	10.07

LIMONENE AND GLACIAL ACETIC ACID AND ANHYDROUS HYDROGEN CHLORIDE

Date	1 Vol. of Limonene + 1 Vol. of Acid + 1.11 gms. of H Cl.			1 Vol. of Limonene + 2 Vols. of Ac. + 1.11 gms. of H Cl.		
	$D_{20°}$	$(\alpha)_{20°}$	p. c. limonene as ester	$D_{20°}$	$(\alpha)_{20°}$	p. c. limonene as ester
May 15, 1907.	0.9408	+46° 45′	2.78	0.9754	+31° 25′	3.78
Dec. 7, 1909.	0.9430	+46° 16′	7.47	0.9770	+30° 20′	9.39

LIMONENE AND GLACIAL ACETIC ACID AND ANHYDROUS SODIUM ACETATE

Date	1 Vol. of Lim. + 1 Vol. of Acid + 2.5 gms. of Na $OCOCH_3$			1 Vol. of Lim. + 2 Vols. of Acid + 2.5 gms. of Na $OCOCH_3$		
	$D_{20°}$	$(\alpha)_{20°}$	p. c. limonene as ester	$D_{20°}$	$(\alpha)_{20°}$	p. c. limonene as ester
May 15, 1907.	0.9490	+45° 15′	5.19	0.9798	+31° 12′	5.70
Dec. 7, 1909.	0.9700	+35° 45′	33.30	0.9870	+28° 58′	15.95

AMYLENE AND GLACIAL ACETIC ACID

Date	1 Vol. of Amylene + 1 Vol. of Acid			1 Vol. Amylene + 2 Vols. Acid		
	$D_{20°}$		p. c. amylene as ester	$D_{20°}$		p. c. amylene as ester
May 20, 1907.	0.8640	.....	7.90	0.9253	.....	7.58
Dec. 7, 1909.	0.9560	.....	23.00	0.9910	.....	33.80

Taken as a whole the changes which have taken place in these mixtures in the last two and one-half years have been largely in the direction indicated by the observations made during the first five months. In the mixtures of pinene and glacial acetic acid the specific gravity has continued to increase very gradually while the angle of rotation has decreased to about one-half in both mixtures. The amount of esters has also very materially increased.

In the mixtures of limonene and glacial acetic acid similar changes as indicated in the pinene mixtures have taken place but to a much smaller extent. In those mixtures containing hydrogen chloride as a catalytic agent the changes, though in the same direction as indicated previously have been very small indeed. A much higher formation of esters and a correspondingly greater change in the physical constants has taken place in the mixture of limonene and acetic acid containing anhydrous sodium acetate. This is especially true where equal parts of acid and hydrocarbon are used. It seems that here the catalytic action of the sodium acetate has exerted a very strong influence. The mixtures of amylene and acetic acid show a very considerable increase in specific gravity and a large amount of ester.

In commenting on the results obtained in the first few months, attention was directed to the apparent influence of mass action. The extent of ester formation was in almost every case greater where the amount of the acid was doubled. This influence of mass action is much less evident after the recent examination. Yet it remains apparent in the mixtures of pinene and acetic acid, in the mixtures of limonene and acetic acid with the anhydrous hydrogen chloride, and in the mixtures of amylene and acetic acid. On the other hand in the case of limonene and acetic acid and limonene and acetic acid with the anhydrous sodium acetate the indication is in the opposite direction. The latter mixture, even during the first five months showed that the amount of ester formed, where the volume of acetic acid was doubled, was practically the same as where equal volumes of the acid and limonene were used. Now, after a much longer period of contact it is found that the mixture of equal volumes shows 33.3 p. c. of limonene changed to esters and the mixture

where the acid was doubled only 13.95 p. c. In these same mixtures the higher per cent of esterification is accompanied by a correspondingly greater change in the physical constants. It seems then that nothing definite can be said about the influences of mass action, especially in mixtures containing limonene to which catalytic agents have been added. On the other hand, in mixtures of pinene and also those of amylene the effect of mass action seems to be quite clearly indicated.

The physical constants show, on the whole, very consistent changes. The specific gravity has steadily increased in all cases and the angle of rotation decreased. It is also seen that in the majority of cases, and this is especially true of the angle of rotation, the extent of the change is largely in proportion to the amount of ester formed.

REVIEW OF LITERATURE

Bouchardat et Lafont, 1886. Sur Une Nouvelle Synthèse D'un Bornéol Inactif. Compt. Rend., 102, p. 171

A mixture of one part of turpentine oil and one and one-half parts of glacial acetic acid was heated for 36 hours at 100°. The mixture was agitated with water, then with a solution of an alkali and finally submitted to fractional distillation. The products of the distillation were: pinene boiling at 156° and another product boiling at 215°. Under the above conditions only a small amount of pinene is combined. If the mixture is heated to 150° the reaction is greatly increased, and a substance boiling at 215° is obtained. This is the acetic ester of borneol. It is a white mobile liquid with an odor reminding of thyme, optically inactive, with a specific gravity of 0.977 at 0° C. Upon heating for six hours in a sealed tube with alcoholic potassa it is saponified and inactive borneol is formed.

Bouchardat et Lafont, 1886. Sur L'action de l'acide Acétique Sur L'essence de Térébenthine. Compt. Rend., 102, p. 318. [Jour. Chem. Soc., 50, p. 475.]

In the experiments performed with pinene and acetic acid the following facts were brought out:

Acetic acid combines with pinene in the cold forming the monoacetates, belonging to two distinct series. At the same time the pinene not combined is changed to two isomeric hydrocarbons $C_{10}H_{16}$, one "monovalent," i. e. "térébenthène," with one double bond; and the other "bivalent," i. e. "terpilène," with two double bonds.

Bouchardat et Lafont, 1886. Formation D'alcools Monoatomiques Dérivés de L'essence de Térébenthine. Compt. Rend., 102, p. 433

From French turpentine two acetates were obtained with the same empirical formulas, $C_{10}H_{16}(C_2H_4O_2)$, but with widely different properties. From these acetates the two corresponding alcohols were obtained. Both alcohols have the formula

$C_{10}H_{18}O$, but their properties are totally different. The method of obtaining the acetates was as follows: The mixture of the compounds resulting from the turpentine oil and acetic acid was warmed with its weight of potassa and five or six times its weight of alcohol in a sealed tube at 100°C. for 10 hours. Upon the addition of water an oily layer separated which was purified by redistillation.

The following tabulation shows the acetates that were obtained and the products which they yielded upon saponfication:

Acetate formed	B. P.*	$(\alpha)_D$	Alc. formed on saponification	B. P.*	(α)
$C_{10}H_{16}(C_2H_4O_2)$.....	95–105°	+1° 16′	Terpilenol.....	99–102°	—17° 24′
Acetate de térébenthine....	105–110°	.....	Terpilenol camphenol...	.....	—43° 6′
Acetate de terpilène.....	110–116°	.....	Terpilenol.....	99–105°	Active

* Under diminished pressure, "dans le vide."

From the alcohol obtained from the first acetate in the table a crystalline substance separated which was dried on porous plate. It was found to be laevogyrate borneol. It is observed that there is a more abundant production of laevogyrate borneol than of dextrogyrate borneol.

Lextrait. Action de L'acide Picrique Sur le Térébenthène, et sur le thymène. Compt. Rend., 102, p. 555 [Ber. 19, p. 237, Ref.]

Picric acid does not act on pinene or oil of turpentine in the cold, but at 150° vigorous action sets in. Upon cooling, yellow crystals separate which can be washed with hot alcohol. These crystals have the formula: $C_{10}H_{16}C_6H_2(NO_2)_3OH$. The crystals are insoluble in water but soluble in boiling alcohol and ether. Upon boiling with caustic potash they yield borneol as a white precipitate. This borneol has a melting point 199°–200° and boils at 211°; α_D =—37°. With HCl it gives a compound decomposible by boiling water; and with nitric acid a substance which corresponds with ordinary camphor in odor, composition, boiling and melting point.

Bouchardat et Lafont, 1891. Action de L'acide Benzoique Sur L'essence de Térébenthine. Compt. Rend., 113, p. 551

Benzoic acid acts slowly on turpentine oil in the cold. Upon heating to 150° the reaction is more rapid. After heating for 50 hours all the oil is changed. It is best not to let the temperature go much above 150°. The operation is best carried out by heating in a copper vessel with a reflux condenser.

The products formed are numerous. Any excess of acid is taken out with an alkaline solution. It is then distilled up to

It is supposed that the benzoate of pinene is first formed which upon the prolonged heating decomposes into camphene and terpilene.

200°–220°. The products of the fractionation are:

1. Camphene $\alpha_D = -3°30'$ b. p. 157°
2. Terpilene $\alpha_D = -3°$ to 4°30′ b. p. 175°–180°

Tilden and Forster, 1893. Preparation of Bornyl Picrate. Journ. Chem. Soc., 1893, 1, p. 1388. [Ber. 37, p. 136, Ref.]

Picric acid is heated with ten times its weight of pinene to 150°. The reaction keeps the temperature up. Some water is produced and some of the acid changes to a tarry mass. When the excess of the acid begins to solidify the dark brown liquid is decanted into a beaker and after several hours tufts of yellow crystals form. These are washed with cold alcohol, and then crushed with water in a mortar as long as the latter turns yellow. They are then recrystallized several times from hot alcohol; m. p. 133°.

The picrate obtained from American turpentine oil was identical with that obtained from French turpentine. The latter yielded a borneol which was leavo, while the former yielded an inactive borneol. When the picrate was heated alone a distillate was obtained which solidified and was found to be camphene; m. p. 47°.

Bouchardat et Tardy, 1895. Sur les Alcools Dérivés d'un Térébinthène droit, L'eucalyptène. Compt. Rend., 120, p. 1417.

Voiry has made known the presence of small quantities of a strongly dextrogyrate terpene in the oil of *Eucalyptus globulus* distilled in France. This terpene, after numerous rectifications,

had an optical rotation of +34°10′ in a 100mm tube. The terpene obtained from the same species of Eucalyptus but from a different province was almost entirely inactive. This terpene is considered to be a mixture of a dextro and a levo terpene which makes it entirely or almost entirely inactive. A terpene, –40°30′, was transformed into terpineol formate by acting on it with crystallized formic acid in the cold. This was then saponified and upon distillation yielded an oil which solidified in a freezing mixture. The terpineol m. p. 33°–34° thus prepared has all the properties of that obtained from laevo-pinene.

Borneol and iso-borneol were prepared from this "eucalyptene" by heating with benzoic acid to 150°. Most of the terpene is changed to dextro limonene. Another part formed the benzoic ether of a dextro borneol and of the optical isomer iso-borneol or fenchol. The dextro borneol obtained in this method possessed optical peculiarities but rarely observed by the author in connection with the other synthetic borneols. Its melting point, after numerous crystallizations from petroleum ether and carbon disulphide, was in the neighborhood of 213°. Its angle of rotation was +18°40′ whereas that of the camphor which it yielded was +31°.

The fenchol or iso-borneol obtained was separated by a series of distillations and crystallizations Its m. p. was 45° and b. p. about 198°–200°. It has all the properties of iso-borneol prepared from laevo pinene. It furnishes a d-camphor upon oxidation which is liquid at 15°, solid at 0°. It is strongly dextrogyrate and seems to be identical with anise camphor of Landolph or the fenchone of Wallach.

Kriewitz, O., 1899. Ueber Addition von Formaldehyd an enige Terpene. Ber., 32, p. 57

Twenty gms. of the pinene fraction of American turpentine oil, 4.4 gms. of paraformaldehyde and 10 gms. of alcohol are heated in a sealed tube to 170°–175° for about 12 hours. After cooling water is added and an oily layer separates which is shaken out with ether. Upon fractionation a large quantity of turpentine comes over. Fraction 225°–240° is rectified with steam. The oily distillate is shaken out with ether and after

the evaporation of the ether the oil remaining is fractionated and fraction 232°–236° is collected. It is a clear liquid of a somewhat thick consistance with an oder reminding of turpentine. It is insoluble in water but soluble in ether, alcohol, and ligroin. It is very hygroscopic, strongly dextrogyrate, and has a specific gravity of 0.9610 at 20°C. The yield is very small, being only about 15 per cent. of the pinene used. The compound was found upon analysis to have the formula $C_{11}H_{18}O$. It adds two molecules of hydrogen chloride, hence is unsaturated. That an alcohol group results is revealed by the formation of an acetyl and a benzoyl compound.

Dextro limonene and dipentene form similar addition products with formaldehyde.

Wallach, O., 1901. Reobachtungen in der Fenchen Riehe. Ann. 315, p. 273

Mix 20 gms. of fenchene with 40 gms. of alcohol and 7 cc. of dilute sulphuric acid and heat it on a water bath for some hours. Only a small quantity of fenchene is recovered and in its place a number of higher boiling compounds are formed. Fraction 200°–201° was found to have the formula $C_{10}H_{17}OC_2H_5$ or ethyl ether of iso-fenchyl alcohol.

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